IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Stoyanov et. al.

Attorney Docket No. 25277

Application No. 10/748,930 Group Art Unit: 1731

Filed: 12/30/03 Examiner: Cordray, Dennis R.

Title: Individualized Intrafiber Crosslinked Cellulosic Fiber With Improved Brightness and Color

DECLARATION OF ANGEL STOYANOV PURSUANT TO § 37 C.F.R. § 1.132

Federal Way, WA,
March 17, 2008

TO THE COMMISSIONER OF PATENTS:

I, Angel Stoyanov, declare and state as follows:

1. I am currently employed by the Weyerhaeuser Company as a Scientist and since 1998 have worked exclusively on crosslinking of cellulosic fibers.

2. I received my Bachelor of Science and my Master of Science from the University of Chemical Technology and Metallurgy at Sofia, Bulgaria, in 1980 and 1981, respectively. After graduation my work history is as follows:

I was a Research Assistant from 1982 to 1986 and an Assistant Professor from 1986 to 1994 at the University of Chemical Technology and Metallurgy at Sofia, Bulgaria. From 1990 to 1991 I worked under a Fulbright scholarship at the University of Washington, Seattle, WA, and completed all graduate courses for a Ph. D. in 1996. From

1996 to 1998 I conducted research for my Ph. D. and held various teaching positions in the Department of Engineering at the University of Washington.

3. I have read and am familiar with the Hansen et al patents US Patent No. 5,589,256 and US Patent No. 5,789,326.

4. Hansen et al. state in the '256 patent that initial application of the binder on high bulk fibers preferably occurs after the curing step, particularly if the binder is capable of functioning as a crosslinking material. Hansen then states that specific binders that can also crosslink are polyols, polycarboxylic acids and polyamines. If such binders are present during curing, the binder will be consumed during the curing step to form covalently crosslinked bonds. When this occurs, the binder is no longer available for hydrogen bonding or coordinate covalent bonding, and particle binding to fibers is ineffective, column 23, line 4 - 14.

5. Hansen further states that in processes that use polycarboxylic acid, polyols and polyaminesas binders the fibers should contain at least 20 % water (or 20 – 50 % water) by weight if the particles and binder are present in the fibers when curing occurs. The water inhibits covalent bond formation and prevents all of the binder from being used to form covalent intrafiber crosslinks. Hence, some of the binder remains available to form the non-covalent bonds with the particles and produce ease of densification in fiber products made by the process of the invention, column 23, line 21 – 32.

6. Hansen et al. state in the '326 patent that curing in the presence of the binder is not usually a problem because the binder cannot always participate in the crosslinking reaction. Hansen then states that in certain situations the binder can also form covalent intrafiber crosslinks. Polycarboxylic acids (such as citric acid), polyols (such as dipropylene glycol) and polyamines (such as ethylene diamine) can function as crosslinking agents and are consumed during the curing step in the formation of covalent crosslinks. Hansen further states that when the crosslinking agent is also a binder steps should be taken to prevent the binder from being consumed as a crosslinker in the curing step. Hansen found that about 20 % water but more preferably at least 30 % by weight of the fibers will retard curing so that adequate binder functional groups remain available to bind particles to fiber. Hansen states that when curing the crosslinking material in the

presence of a binder that is also a crosslinking material the fibers should contain at least 20 % by weight of the fibers when curing begins, column 46, line 3 – line 26.

7. Tests were undertaken to determine the effect of water addition on curing. Accordingly I planned and supervised experiments which were carried out by my assistant, Kathy Marsh. In the experiments, a polycarboxylic acid (citric acid), a polyol (sorbitol) and a catalyst (sodium hypophosphite) were added to cellulose fibers (CF416 pulp) and air dried. Water at the 20 and 30 % by weight level was added to the air dried samples which were then cured. Comparison was made to samples in which no water was added.

8. Exhibit A shows the experimental design for the tests and the procedure. All samples were cured at 171°C for 7 minutes. The acronyms are as follows: COP, chemical on pulp (CF416 pulp from Weyerhaeuser Co.); SHP, sodium hypophosphite; CA, citric acid; SOR, sorbitol. Exhibit B shows the addition levels for the various reagents; Exhibit C shows the summary of brightness testing by TAPPI T 525 om-02 and the FAQ wet bulk results determined by the procedure in the application. The Hunter color values were determined by TAPPI T 1231 sp 98. Whiteness Index, $WI_{(CDM-L)}$, was calculated from the formula, $WI_{(CDM-L)} = (L-3b)$.

10. The results are summarized in Table 1. It is well recognized by those skilled in the art of crosslinked fibers that an increase in FAQ wet bulk, relative to an untreated control, reflects that fibers have been crosslinked. For reference purposes, an untreated control is Sample A in my earlier Declaration of September 29, 2006 submitted on October 9, 2006 in response to the Examiner's Action dated July 7, 2006.

Table 1
Effect of Water Addition On Crosslinking With A Polycarboxylic Acid In The presence Of A Polyol

VVI (CDM-L)

Sample ID	Chemistry	XLinker	SHP	Sorbitol	Water added	Cure Temp	Cure Time	FAQ Wet Bulk at 0.6 kPa	ISO Brightness	Hunter Space Values			Whiteness Index
										L	A	B	
	–	(% COP)											
A3	CA+polyol	8	2	6	0	340	7	16.49	85.30	95.70	–1.00	4.80	81.30
B3	CA+polyol	8	2	6	20	340	7	16.47	85.20	95.60	–0.90	4.70	81.50
A4	CA+polyol	8	2	6	0	340	7	16.56	85.21	95.73	-1.10	4.92	80.97
B4	CA+polyol	8	2	6	30	340	7	16.45	85.26	95.71	-1.10	4.86	81.13

11. Sample A3 is a control which has been treated with 8 % by weight citric acid crosslinking agent, 2 % by weight sodium hypophosphite and 6 % by weight sorbitol, and then air dried and cured. Sample B3 is treated in the same manner as sample A3 with the exception that 20 % by weight water was added after air drying. Both samples were then cured at 171°C for 7 minutes. Sample A4 is a control which has been treated with 8 % by weight citric acid crosslinking agent, 2 % by weight sodium hypophosphite and 6 % by weight sorbitol, and then air dried and cured. Sample B4 is treated in the same manner as sample A4 with the exception that 30 % by weight water was added after air drying. Both samples were then cured at 171°C for 7 minutes.

12. Based on the fact that there is no decrease in FAQ wet bulk when pulp is treated with citric acid, sodium hypophosphite, sorbitol, air dried and then treated with 20 % and 30 % by weight water, it is my opinion that the crosslinking reaction with citric acid is not affected by the presence of either 20 % or 30 % by weight water prior to curing.

13. In accordance with accepted Patent Office Practice, the dates in the laboratory notebook pages presented in Exhibits A- C have been redacted.

14. I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued therefrom.

Respectfully submitted,

Date 3/17/08

Stoyanov

Angel Stoyanov

15134 Exp. # 157: CA + Polyols for Patent Action (3) [redacted]

XM

Angel

XM

Weyerhaeuser Confidential

Patent Action Due Date: [redacted]

Title: **Experiment # 157: CA + Polyols for Patent action (3)**

Objective(s): Investigate whether the addition of > 20% water prevents the crosslinking with CA in the presence of polyol (Sorbitol)

Materials:

- Pulp: CF416
- Sample size: 20 g
- Xlinker: CA
- Catalyst: SHP
- Polyols: Sorbitol (Sorbidex)
- Fiberizer: 6" pad former
- Dispatch oven
- Metal baskets for curing

Experimental Design:

Sample ID	Chemistry	XLinker	SHP	Sorbitol	Water	Cure Temp.	Cure time
	-	(% COP)	(% COP)		%	(F)	(min.)
A3	CA+SHP+SOR	8	2	6	-	340	7
B3	CA+SHP+SOR	8	2	6	20	340	7

Procedure:

1. Weigh the sample 20 g (odb);
2. Apply the crosslinking solution using the usual syringe method;
3. Leave the samples ~~overnight~~ in a sealed plastic bags;
4. Use the 6" pad former for fluffing (50% consistency);
5. Air dry the samples;
6. Add 20% water by aerosol spraying to Sample B3;
7. Let Sample B3 stay in a plastic bag for 2 h;
8. Cure both samples simultaneously in the Despatch V Series oven;
9. Store the cured fibers in a plastic bag.

Testing:

1. AFAQ Wet Bulk at 0.6 kPa
2. Brightness/Color

XM

XM

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Stanley Marsh [redacted]

EXHIBIT A

5000000\17
15134 Exp. #158: CA + Polyols for [redacted]
Patent Action (4)

XM XM

Weyerhaeuser Confidential

Patent Action Due Date: [redacted]

Title: **Experiment # 158: CA + Polyols for Patent action (4)**

Objective(s): Investigate whether the addition of 30% water prevents the crosslinking with CA in the presence of a polyol (Sorbitol)

Materials:

- Pulp: CF416
- Sample size: 20 g
- Xlinker: CA
- Catalyst: SHP
- Polyols: Sorbitol (Sorbidex)
- Fiberizer: 6" pad former
- Dispatch oven
- Metal baskets for curing

Experimental Design:

Sample ID	Chemistry	XLinker	SHP	Sorbitol	Water	Cure Temp.	Cure time
	-	(% COP)	(% COP)		%	(°F)	(min.)
A4	CA+SHP+SOR	8	2	6	-	340	7
B4	CA+SHP+SOR	8	2	6	30	340	7

Procedure:

1. Weigh the sample 20 g (odb);
2. Apply the crosslinking solution using the usual syringe method;
3. Leave the samples overnight in a sealed plastic bags;
4. Use the 6" pad former for fluffing (50% consistency);
5. Air dry the samples;
6. Add 30% water by aerosol spraying to Sample B4;
7. Let Sample B4 stay in a plastic bag for 2 h;
8. Cure both samples simultaneously in the Despatch V Series oven;
9. Store the cured fibers in a plastic bag.

Testing:

1. AFAQ Wet Bulk at 0.6 kPa
2. Brightness/Color

 APS [redacted]

XM XM

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Kathy Marsh [redacted]

EXHIBIT B

Exp. # 157 (cont.) 15134

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KM KM

Exp. # 157 [redacted]

		target	actual	pH	actual
A3	8% CA	3.2 g	-	-	-
	2% SHP	0.964			
	6% SOR	2.4			
	40 mls H_2O	40			
B3	8% CA	3.2 g	-	-	-
	2% SHP	0.964			
	6% SOR	2.4			
	40 mls H_2O	40			
	[20% H_2O]				
Master Batch	CA	6.4 g	6.400	2.04	2.04
	SHP	1.928	1.929		
	SOR	4.8	4.804		
	H_2O	80	80.000		

	pulp	+ 20 ml solution
A3	20.02 g	40.86 g
B3	19.90 g	39.42

20% H_2O B3

dry wt. 22.24 g

20% = 4.45

26.69 ~ 27 g

KM KM

Kathy Marsh [redacted]

EXHIBIT B

Project No.
Book No. 15134 TITLE Exp. #157 (cont.)
61

XM XM

Sorbitol
CA
SHP } Same as Exp. #154

Applied 20 g solution via syringe method [redacted]
Equilibrate overnight.
Fiberized in 6" pad former - 1 pass [redacted]
Dry overnight
Sprayed sample B3 with H_2O - sit 2 hours. [redacted]
Cure in Despatch oven - A3 in ½ of basket,
B3 in other half with pulp sheet divider -
340°F for 3.5 min, turn basket, 3.5 min longer.

XM XM

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EXHIBIT C

ads

ample ID	side	position	TEST DATE	BRIGHTNESS	L	a	b	L*	a*	b*
A3	a	1	[redacted]	85.72	95.92	-0.93	4.79	96.82	-0.89	4.74
	a	2		85.17	95.67	-0.94	4.83	96.62	-0.9	4.79
	a	3		85.21	95.71	-0.92	4.86	96.68	-0.89	4.81
	b	1		85.23	95.65	-0.98	4.78	96.61	-0.94	4.74
	b	2		85.27	95.72	-1.03	4.81	96.66	-0.99	4.77
	b	3		85.33	95.69	-0.94	4.76	96.64	-0.91	4.71
			Average	**85.32**	**95.73**	**-0.96**	**4.81**	**96.7**	**-0.9**	**4.8**
			StDev	**0.2**	**0.1**	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**
B3	a	1	[redacted]	85.37	95.7	-0.9	4.69	96.65	-0.86	4.64
	a	2		85.18	95.62	-0.91	4.7	96.59	-0.87	4.66
	a	3		85.27	95.63	-0.91	4.67	96.59	-0.88	4.62
	b	1		85.27	95.66	-0.85	4.7	96.62	-0.82	4.65
	b	2		84.77	95.34	-0.94	4.65	96.37	-0.9	4.61
	b	3		85.25	95.58	-0.89	4.63	96.55	-0.85	4.58
			Average	**85.19**	**95.59**	**-0.90**	**4.67**	**96.6**	**-0.9**	**4.6**
			StDev	**0.2**	**0.1**	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**

XM

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Understood by me, Date, Invented by
Recorded by Vathy Marsh [redacted]

EXHIBIT B

Exp. # 158 (Cont.) 15134

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KM KM

Exp. # 158 [redacted]

(Same as Exp. # 157)

Master Batch		target	actual	pH
	CA	6.4 g	6.401	2.00
	SHP	1.928	1.928	
	SOR	4.8	4.801	
	H_2O	80	80.005	

		pulp wt.	+ 20 ml solution
(1)	A4	20.12 g	40.14 g
(2)	B4	20.06	40.07

30% H_2O B4 dry wt. 22.24

30% 6.67

28.91 ~ 29

Sorbitol
CA
SHP
} Same as Exp. # 154

Apply solution via syringe. [redacted]

Equilibrate overnight.

Fiberize in 6" pad former - 1 pass. [redacted]

Dry overnight. [redacted]

Spray ~~B3~~ B4 with H_2O, equilibrate + cure (Same as Exp. # 157)

KM KM

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Kathy Marsh [redacted]

EXHIBIT C

Exp. #157 (cont.) Book No. 15134
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KM KM

FAQ

Test Date	Ref # or Jumbo #	Sample Number	Pulp Grade	Operator Initial	Lab Name	Run Number	Dry Bulk 0.6kPa cc/g	Dry Bulk 2.5kPa cc/g	Wick Time sec	Wick Rate mm/s	Wet Bulk 2.5kPa cc/g	Wet Bulk 0.6kPa cc/g	Absorb Capacity g/g
[redacted]	AS-X157	A3	CA+SHP+SOR	Deb	Lab 116	1	44.67	24.71	2.3	13.07	13.86	16.56	16.58
	AS-X157	A3	CA+SHP+SOR	Deb	Lab 116	2	45.95	28.31	2.3	13.61	13.88	16.56	16.55
	AS-X157	A3	CA+SHP+SOR	Deb	Lab 116	3	45.37	25.99	2.3	13.48	13.8	16.36	16.27
	AS-X157	A3	CA+SHP+SOR	Deb	Lab 116	AV	45.33	25.67	2.3	13.39	13.84	16.49	16.46
	AS-X157	B3	CA+SHP+SOR	Deb	Lab 116	1	44.79	25.54	2.7	11.33	13.73	16.36	16.39
	AS-X157	B3	CA+SHP+SOR	Deb	Lab 116	2	45.82	26.44	2.8	11.21	13.86	16.49	16.66
	AS-X157	B3	CA+SHP+SOR	Deb	Lab 116	3	44.99	26.08	2.6	11.98	13.93	16.58	16.64
	AS-X157	B3	CA+SHP+SOR	Deb	Lab 116	AV	45.2	26.01	2.7	11.61	13.84	16.47	16.56

KM KM

KM KM

Experiment #157: CA and Polyols for Patent Action (3)
3/5/2008

Sample ID	Chemistry	Xlinker	SHP	Sorbitol	Amount Water (%)	Cure Temp (°F)	Cure Time (min)	Dry Bulk 0.6kPa cc/g	Dry Bulk 2.5kPa cc/g	Wick Time sec	Wick Rate mm/s
A3	CA+SHP+SOR	8	2	6	0	340	7	45.33	25.67	2.3	13.39
B3	CA+SHP+SOR	8	2	6	20	340	7	45.20	26.01	2.7	11.51

KM KM

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Sample ID	Wet Bulk 2.5kPa cc/g	Wet Bulk 0.6kPa cc/g	Absorb Capacity g/g	Brightness (%)	Color Hunter L	Color Hunter a	Color Hunter b	Color CIE L*	Color CIE a*	Color CIE b*
A3	13.84	16.49	16.46	85.3	95.7	-1.0	4.8	96.7	-0.9	4.8
B3	13.84	16.47	16.56	85.2	95.6	-0.9	4.7	96.6	-0.9	4.6

KM KM

To Page No. X

Kathy Marsh [redacted]

EXHIBIT C

Project No
Book No. 15134 TITLE Exp #158 (cont.)
From Page No. 65

XM FAQ XM

Test Date	Ref # or Jumbo #	Sample Number	Operator Initial	Lab Name	Run Number	Dry Bulk 0.6kPa cc/g	Dry Bulk 2.5kPa cc/g	Wick Time sec	Wick Rate mm/s	Wet Bulk 2.5kPa cc/g	Wet Bulk 0.6kPa cc/g	Absorb Capacity g/g
[redacted]	AS-X158	A4	Deb	Lab 116	1	45.89	26.38	2.6	12.06	13.86	16.62	16.59
	AS-X158	A4	Deb	Lab 116	2	45.5	26.44	2.6	12.1	13.93	16.56	16.68
	AS-X158	A4	Deb	Lab 116	3	45.63	26.76	2.7	11.74	13.93	16.49	16.43
	AS-X158	A4	Deb	Lab 116	AV	**45.67**	**26.53**	**2.63**	**11.97**	**13.91**	**16.56**	**16.57**
[redacted]	AS-X158	B4	Deb	Lab 116	1	45.24	26.25	2.7	11.59	13.93	16.56	16.68
	AS-X158	B4	Deb	Lab 116	2	43.25	25.35	2.6	11.71	13.73	16.43	16.61
	AS-X158	B4	Deb	Lab 116	3	44.73	25.8	2.7	11.41	13.73	16.36	16.52
	AS-X158	B4	Deb	Lab 116	AV	**44.41**	**25.8**	**2.67**	**11.57**	**13.8**	**16.45**	**16.6**

XM

Tech Deb

EXP	Sample ID	side	position	TEST DATE	BRIGHTNESS	L	a	b	L*	a*	b*
AS-X 158	A4	a	1	[redacted]	85.05	95.73	-1.09	5.03	96.67	-1.06	4.99
		a	2		85.08	95.64	-1.1	4.88	96.6	-1.06	4.84
		a	3		85.04	95.67	-1.12	4.97	96.63	-1.07	4.93
		b	1		85.36	95.78	-1.11	4.89	96.71	-1.07	4.85
		b	2		85.27	95.72	-1.08	4.85	96.66	-1.03	4.81
		b	3		85.47	95.81	-1.09	4.87	96.74	-1.04	4.82
				Average	**85.21**	**95.73**	**-1.10**	**4.92**	**96.7**	**-1.1**	
				StDev	**0.2**	**0.1**	**0.0**	**0.1**	**0.1**	**0.0**	
	B4	a	1	[redacted]	85.32	95.71	-1.04	4.78	96.66	-1	4.74
		a	2		85.34	95.76	-1.04	4.86	96.69	-1	4.82
		a	3		85.21	95.66	-1.06	4.83	96.62	-1.02	4.79
		b	1		85.2	95.7	-1.14	4.87	96.65	-1.1	4.82
		b	2		85.18	95.71	-1.17	4.94	96.66	-1.13	4.89
		b	3		85.31	95.72	-1.13	4.86	96.67	-1.08	4.81
				Average	**85.26**	**95.71**	**-1.10**	**4.86**	**96.7**	**-1.1**	
				StDev	**0.1**	**0.0**	**0.1**	**0.1**	**0.0**	**0.1**	

XM XM

Experiment #158: CA and Polyols for Patent Action (4)

3/5/2008

Sample ID	Chemistry	Xlinker	SHP	Sorbitol	Amount Water (%)	Cure Temp (°F)	Cure Time (min)	Dry Bulk 0.6kPa cc/g	Dry Bulk 2.5kPa cc/g	Wick Time sec	Wick Rate mm/s
A4	CA+SHP+SOR	8	2	6	0	340	7	45.67	26.53	2.63	11.97
B4	CA+SHP+SOR	8	2	6	30	340	7	44.41	25.80	2.67	11.57

XM XM

Wet Bulk 2.5kPa cc/g	Wet Bulk 0.6kPa cc/g	Absorb Capacity g/g	Brightness (%)	Color: Hunter L	Color: Hunter a	Color: Hunter b	Color: CIE L*	Color: CIE a*	Color: CIE b*
13.91	16.56	16.57	85.2	95.7	-1.1	4.9	96.7	-1.1	4.9
13.80	16.45	16.60	85.3	95.7	-1.1	4.9	96.7	-1.1	4.8

XM XM

Date Recorded By: [redacted]